J Therm Anal Calorim (2015) 121:545–546
DOI 10.1007/s10973-015-4636-7

# Comments on the paper "Growth and characterization of semi-organic nonlinear optical crystal: urea thiourea cadmium sulfate"

**Bikshandarkoil R. Srinivasan**[1] · **Zbigniew Tylczyński**[2]

Received: 16 January 2015 / Accepted: 8 March 2015 / Published online: 19 March 2015


**Abstract** The authors of the title paper (Hanumantharao and Kalainathan in J Therm Anal Calorim 114:239–243, 2013) claim to have grown a novel nonlinear optical urea thiourea cadmium sulfate crystal, represented by no molecular formula but by a code UTCS. Using the title crystal as an example, we wish to express the necessity of reporting molecular formula for new compounds and not abbreviations like UTCS.

**Keywords** Molecular formula · Urea thiourea cadmium sulfate · Nonlinear optical · Dubious crystal

During the course of a literature survey of metal complexes containing both thiourea and urea ligands, we came across the title paper by Hanumantharao and Kalainathan reporting on the growth of single crystals of 'urea thiourea cadmium sulfate' by the slow evaporation method [1]. Although the authors claim to have characterized 'urea thiourea cadmium sulfate' (**1**) with the aid of single-crystal and powder X-ray diffraction, infrared and UV–visible spectra, thermal studies, etc., no molecular formula is reported in the entire paper for the so-called novel nonlinear optical (NLO) 'urea thiourea cadmium sulfate crystal'. Instead an abbreviation UTCS is used to represent compound **1** in the title paper. We are of the opinion that abbreviations or codes should not be used as alternates for molecular formula of new compounds. In this case, the name of the title crystal is also not in accordance with standard chemical nomenclature. The same authors had earlier reported growth of another novel crystal with the name thiourea urea zinc sulfate, and this claim has already been proved to be erroneous [2]. Such contradictory names only indicate that the nomenclature employed by the authors is arbitrary.

We believe that the authors named the title crystal based on an incorrect assumption that the slow evaporation of an aqueous solution containing urea, thiourea, and cadmium sulfate in equimolar ratio will result in the formation of a so-called UTCS crystal. The characterization of the UTCS crystal is not based on a correct interpretation of the diffraction and spectral data, as can be evidenced from the reported infrared (IR) spectral and X-ray diffraction results. Although the authors state '*FTIR spectra show the characteristic vibration frequencies of urea and thiourea. This confirms the formation of UTCS compound*,' a scrutiny of the reported infrared spectrum rules out the presence of any urea due to the absence of the carbonyl of the C=O vibration, which is expected as an intense signal. The authors have not assigned any C=O vibration and did not think it is important to look for this strong signal in a supposedly urea-containing compound as suggested by the name. Based on the IR spectrum, it can be concluded that the name 'urea thiourea cadmium sulfate' is inappropriate for the UTCS crystal. The same criterion namely the absence of the C=O vibration was used as evidence to prove the dubious nature of five other improperly characterized compounds (Table 1) claimed to contain both urea and thiourea [2–4].

In their discussion of single-crystal X-ray diffraction, the authors state '*UTCS belongs to triclinic system and crystallizes in space group "P1" with cell parameters*

✉ Zbigniew Tylczyński
zbigtyl@amu.edu.pl

Bikshandarkoil R. Srinivasan
srini@unigoa.ac.in

[1] Department of Chemistry, Goa University, Goa 403206, India

[2] Faculty of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznan, Poland

**Table 1** List of improperly characterized metal–urea thiourea compounds

| No. | Name and code | Actual compound | Refs. |
|---|---|---|---|
| 1 | Thiourea urea zinc sulfate (TUZS) | Tris(thiourea) zinc(II) sulfate | [2] |
| 2 | Thiourea urea magnesium chloride (TUMC) | Thiourea | [3] |
| 3 | Urea thiourea sodium chloride (UTNC) | Thiourea | [3] |
| 4 | Urea thiourea mercuric chloride (UTHC) | Bis(thiourea) mercury(II) chloride | [4] |
| 5 | Urea thiourea mercuric sulfate (UTHS) | Bis(thiourea) mercury(II) sulfate | [4] |
| 6 | Urea thiourea cadmium sulfate (UTCS) | Tris(thiourea) cadmium sulfate | This work |

$a = 9.02$ Å, $b = 10.95$ Å, and $c = 7.02$ Å; $\alpha = 92.41°$, $\beta = 116.27°$, $\gamma = 90.99°$'. The reason for assignment of the *P1* space group is not given, and it is not clear whether the space group was assigned based on structure refinement. The results of the single-crystal work are unacceptable due to the absence of a CIF file to substantiate the same. The authors have not taken into consideration the known literature of the thiourea compounds of Cd as it is well documented that $CdSO_4$ forms with thiourea three different complexes, which can be obtained from aqueous solutions of the components by varying their ratios [5]. The 1:1 Cd–thiourea compound $[Cd(tu)(SO_4)(H_2O)_2]$ (tu = thiourea) crystallizes in the centrosymmetric orthorhombic *Pbca* space group [5], while the 1:3 compound $[Cd(tu)_3(SO_4)]$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ having unit cell parameters $a = 8.77(2)$, $b = 9.05(2)$, $c = 9.83(1)$ Å, $a = 91.3(2)°$, $\beta = 111.9(1)°$, $\gamma = 95.5(2)°$ [6]. Although these data appear the closest to the cell reported (without any esd values) in the title paper, UTCS should be declared as a dubious crystal in view of (1) the absence of structure refinement details, (2) non-reporting of any chemical composition, and (3) claim of using equimolar ratios of $CdSO_4$ and tu for crystal growth. For a dubious crystal (UTCS), studies such as thermal analysis and NLO property are meaningless and hence are not commented. The title crystal is a new member of the growing list of improperly characterized metal–urea thiourea compounds.

In summary, the improperly characterized urea thiourea cadmium sulfate crystal without a molecular formula cannot be termed as a novel compound.



## References

1. Hanumantharao R, Kalainathan S. Growth and characterization of semi-organic nonlinear optical crystal-urea thiourea cadmium sulfate. J Therm Anal Calorim. 2013;114:239–43.
2. Srinivasan BR, Naik TA, Tylczyński Z, Priolkar KR. Reinvestigation of growth of thiourea urea zinc sulfate crystal. Spectrochim Acta. 2014;117A:805–9.
3. Srinivasan BR. On the existence of 'thiourea urea magnesium chloride' and 'urea thiourea sodium chloride'. J Therm Anal Calorim. 2015;119:985–8.
4. Srinivasan BR, Fernandes R. Comments on the paper: 'Crystal growth and comparison of vibrational and thermal properties of semi-organic nonlinear optical materials'. Pramana J Phys. 2015 (accepted).
5. Cavalca L, Domiano P, Gasparri GF, Boldrini P. The crystal structure of monothiourea-cadmium sulphate dihydrate. Acta Crystallogr. 1967;22:878–85.
6. Cavaica L, Villa AC, Mangia A, Palmeiri C. The crystal structure of tris(thiourea)cadmium Sulphate. Inorg Chim Acta. 1970;4:463–70.